^{13}C NMR spectroscopic studies of C-nitroso compounds. The orientation of the nitroso group in substituted nitrosobenzenes

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This paper is dedicated to Professor John C. Polanyi on the occasion of his 65th birthday

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The carbon-13 chemical shifts of several substituted nitrosobenzenes are reported. It is shown that the NO group can be orientated to lie in the plane of the ring when constrained either by a bulky *ortho* substituent or in the solid state. In the presence of 2,6-di-*tert*-butyl substituents the NO group is twisted into orthogonality with the ring. The changes in the ^{13}C chemical shifts are larger for the NO group than for other functional groups. It is suggested that these effects are a consequence of the electronic character of the NO group and that the nitrogen lone pair of electrons is of fundamental importance in producing these unique effects. The dimeric nitroso functional group does not display these properties.

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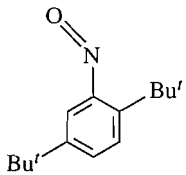
On a mesuré les déplacements chimiques en RMN du ^{13}C de plusieurs nitrosobenzènes substitués. On montre que, sous l'influence d'un substituant *ortho* volumineux ou à l'état solide, le groupe NO peut être orienté de façon à se trouver dans le plan du noyau. En présence de substituants 2,6-di-*tert*-butyles, le groupe NO est déplacé et il est alors orthogonal au noyau. Les changements dans les déplacements chimiques du ^{13}C sont plus importants avec le groupe NO qu'avec d'autres groupes fonctionnels. On suggère que ces effets sont une conséquence du caractère électronique du groupe NO et que la paire libre d'électrons de l'azote est d'une importance fondamentale dans la production de ces effets uniques. Le groupe fonctionnel nitroso dimère ne présente pas ces propriétés.

[Traduit par la rédaction]

Introduction

Over 20 years ago, Okazaki and Inamoto (1) studied the ^{1}H nmr spectra of *ortho*-substituted nitrosobenzenes. Their studies demonstrated that the chemical shifts of aromatic, methyl, methoxyl, and *tert*-butyl protons at the *ortho* positions are abnormal. They suggested that most of the unsymmetrically substituted nitrosobenzenes exist as a conformer where the oxygen atom of the nitroso group is on the opposite side (*anti*) to the substituent, and hence protons in the same side (*syn*) to the nitroso oxygen show unusually high chemical shifts and those *anti* to the nitroso oxygen exhibit unusually low chemical shifts. They showed that in 2,5-di-*tert*-butylnitrosobenzene the molecule existed almost entirely as conformer **1** whereas for other *ortho*-substituted nitrosobenzenes there was an equilibrium between the forms **2***a* and **2***b* (R = Me, MeO, Cl, Br) with the



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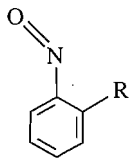
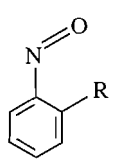


2*a*



2*b*

form **2***a* predominating, particularly at low temperature. A similar conclusion had been reached by Sundberg (2) for R = Me, *n*Pr, *n*Bu. Okazaki and Inamoto extended their studies to the case of 2,4,6-tri-*tert*-butylnitrosobenzene (TBNB) where the chemical shifts of the *ortho tert*-butyl protons were interpreted in terms of the NO group being considered to be almost perpendicular to the plane of the benzene ring. This orthogonality of the NO group has also been invoked by Barclay in photochemical and other studies of TBNB (3, 4).

Because of our interest in the ^{13}C nmr spectra of substituted nitrosobenzenes (5), and the information available in the literature for the ^{13}C nmr effects of freezing out of the rotation of the NO group in nitrosobenzene (6) and of substituted *p*-nitrosoanilines (7, 8) at low temperatures, we embarked on the studies reported here. Subsequently we extended our studies to the coordination chemistry of C-nitrosoarenes (9, 10). A publication on the solid state ^{13}C CP/MAS nmr spectrum of *p*-nitrosodimethylaniline (11) has complemented our study.

In our earlier study (5) we noted the unique effect of the NO group in that its powerful π-electron-accepting property enabled it to dominate other electron-accepting groups in the *para* position of the ring and produce in them electron-donating properties. The monomeric nitroso group has long been realised (12) to be very different in character from the *cis* and *trans* dimeric $-N_2O_2$ functions. These differences are reflected in the very different substituent chemical shifts exhibited by nitrosobenzene and the two dimeric forms (13, 14).

Throughout this paper we shall refer to all aromatic nitroso compounds as derivatives of nitrosobenzene and hence adopt the numbering system based upon **3**. The steric effects of the

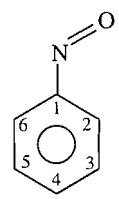


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TABLE 1. Carbon-13 chemical shifts for ring carbons in substituted nitrosobenzenes (20°C, $CDCl_3$ solvent unless otherwise stated)

Substituent(s)	State	C-1	C-2	C-3	C-4	C-5	C-6
2-Iodo	Solution	162.1	109.2	141.4	136.6	128.2	109.0
2-Methyl	Solution	164.9	142.1	132.9	136.1	125.6	107.3
2-Methoxy	Solution	162.0	158.8	115.3	138.8	119.6	108.8
2-*tert*-Butyl	Solution	165.7	152.2	125.8	135.4	127.7	106.5
2-Methyl-6-*tert*-butyl	Solution	167.5	118.0	125.4	130.7	133.4	153.6
2,5-Di-*tert*-butyl	Solution	165.9	148.9	127.6	132.3	149.7	103.3
2,6-Di-*tert*-butyl	Solution	176.3	142.4	125.7	129.9	125.7	142.4
2,4,6-Tri-*tert*-butyl	Solid state	174.5	141.9	122.1	151.2	122.1	141.9
	Solution	173.5	142.8	122.7	153.4	122.7	142.8
	Solution[a] (20°C)	174.5	143.5	123.5	154.2	123.5	145.5
	Solution[a] (0°C)	174.3	143.3	123.4	154.2	123.4	145.3
	Solution[a] (−20°C)	174.0	143.1	123.2	154.0	123.2	143.1
	Solution[a] (−40°C)	173.7	142.9	123.0	153.9	123.0	142.9
	Solution[a] (−60°C)	173.4	142.6	122.8	153.6	122.8	142.6
	Solution[a] (−80°C)	173.4	142.6	122.9	153.7	122.9	142.6
4-Methylamino	Solid state	163.3	109.5	114.6	158.1	114.6	143.1

[a] CD_2Cl_2 solvent.

substituent groups arise therefore from substitution in the 2 and 6 positions.

Experimental

Nitroso compounds

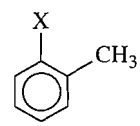
2,4,6-Tri-*tert*-butylnitrosobenzene and *trans*-dimeric 2-methyl nitrosobenzene were commercially available, *trans*-dimeric 2-iodo and 2-methoxynitroso benzene were donated by Professor W. Lüttke, having been prepared by the literature methods (15, 16). 2,5-Di-*tert*-butylnitrosobenzene (17) was prepared by mild oxidation of the corresponding aniline using *m*-chloroperbenzoic acid. 2-*tert*-Butylnitrosobenzene (18) was similarly prepared. 2,6-Di-*tert*-butylnitrosobenzene was prepared in a similar manner to the literature syntheses for other sterically hindered nitrosobenzenes (17). 2,6-Di-*tert*-butylaniline (0.5 g, 2.4 mmol) in dichloromethane (5 cm^3) was cooled in an ice–salt bath while perbenzoic acid (0.6 g, 4.8 mmol) in dichloromethane (5 cm^3) was added dropwise. The reaction mixture was kept overnight at −20°C and a brown colour developed. Column chromatography (silica, petroleum ether 40–60) gave 2,6-di-*tert*-butylnitrosobenzene (0.25 g, 45%) as a blue oil, λ_{max} ($CHCl_3$) 761 nm, ϵ 50.5 $dm^3\ mol^{-1}\ cm^{-1}$; δ_H (200 MHz, $CDCl_3$) 7.25 (3H, m, 3,4,5-H), 1.15 (18H, s, 2,6-di-*t*Bu); *m/z* 219 (M^+ 31%), 57 (*t*Bu, 100%). 2-Methyl-6-*tert*-butylnitrosobenzene was similarly prepared. 2-Methyl-6-*tert*-butyl aniline (1 g, 5.65 mmol) in dichloromethane (10 cm^3) was cooled in an ice–salt bath while perbenzoic acid (1.55 g, 11.0 mmol) in dichloromethane (10 cm^3) was added dropwise. The reaction mixture was kept overnight at −20°C, then neutralised with $NaHCO_3$ solution. Removal of the solvent using a rotary film evaporator at room temperature left a green oil that was purified by column chromatography as above, giving 2-methyl-6-*tert*-butylnitrosobenzene as a blue oil, λ_{max} ($CHCl_3$) 789 nm, ϵ 43 $dm^3\ mol^{-1}\ cm^{-1}$; δ_H (200 MHz, $CDCl_3$) 7.6 (1H, dd, 3-H), 7.35 (1H, t, 4H), 6.95 (1H, dq, 5-H), 1.85 (3H, s, CH_3), 1.65 (9H, s, *t*Bu). *trans*-Dimeric 2,6-dimethyl-, 2,6-diethyl-, and 2,6-diisopropylnitrosobenzene were prepared by controlled oxidation of the corresponding amines (18, 19). *p-N*-methylamino nitrosobenzene was donated by Professor F. Bell.

Instrumental

Natural abundance, broad band proton-decoupled ^{13}C nmr spectra were measured using a Bruker WP 200 spectrometer operating at 50.32 MHz, the solvent being either $CDCl_3$ or CD_2Cl_2. The ^{13}C nmr spectra of solid samples were measured by the SERC service at the Industrial Research Laboratories, University of Durham, at 75.431 MHz using cross polarization (CP) magic angle spinning (MAS) and high-power decoupling and also at the University of East Anglia at 50.3 MHz with CPMAS and high-power decoupling.

Results and discussion

The chemical shifts for the ring carbons of substituted monomeric nitrosobenzenes are listed in Table 1 and are considered under two major headings. The first group comprises those molecules with substituents in the 2 position and no substituent at C-6, together with the 2-methyl-6-*tert*-butyl substituents and solid 4-methylaminonitrosobenzene. The second group is restricted to the two examples where both the C2 and C6 positions carry *tert*-butyl groups. These two separate classes are expected to conform to those originally established by Okazaki and Inamoto (1). In the first group the NO is expected to lie in plane with the ring and displaced away from the 2-substituent (I, Me, MeO, *t*-Bu, 2,5-di-*t*-Bu), away from the larger substituent (2-Me-6-*t*-Bu), or in plane with the ring in a solid monomeric compound as noted by Penner and Wasylishen (11) and ourselves (10). The common feature of these spectra is that the C atom to which the NO group lies *syn* has a chemical shift much lower than would be predicted by use of substituent chemical shifts as given by Ewing (20) in combination with those for the NO group (5, 13, 14). This difference between calculated and observed shifts is 12–14 ppm and can best be appreciated by comparison with the calculated values for C-6 in 2-methyl-1-X-benzene, **4** (X = F, Cl, Br, I, NO_2, CHO, CN, OH, COOH, OMe, NH_2, NHEt, Me, Et, *cis*-N_2O_2, *trans*-N_2O_2)



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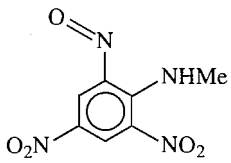
where the difference varies between 4 ppm lower and 2 ppm higher. It is apparent that the effect of the NO group is unique, as suggested by Lunazzi et al. (6). A further example of the effect can be seen from comparison of the predicted and observed chemical shifts for the molecules **5** (21), **6** (22) and **7** (23). The observed C-6 chemical shifts are 110.5, 121.8, and 129.9 respectively.

Comparison of **5** with **6** implies that in the latter the steric restraints are such that the NO group can rotate freely at room temperature whereas in the former the NO group adopts the

TABLE 2. A comparison of substituent chemical shifts in compounds **8** and **9** (all values in ppm)

X	SCS(X) in **8**[a]	SCS(X) in **9**[b]	Difference	Reference
COOH	10.8	2.1	8.7	24
COCl	14.1	5.0	9.1	24
CO_2Me	9.0	2.0	7.0	24
CONHPh	13.1	6.5	6.6	24
$CONMe_2$	10.7	8.1	2.6	24
COEt	17.7	8.8	8.9	24
CHO	17.8	8.4	9.4	25
COMe	18.1	8.9	9.2	26
CN	−13.1	−15.7	2.6	27
OMe	38.0	31.4	6.6	28
Br	2.3	−5.8	8.1	26
NNPh	32.0	24.0	8.0	29
$NNC_6H_2(Bu^t)_3$	35.3	25.1	10.2	29
NH_2	21.7	18.2	3.5	[d]
NMe_2	31.9	22.5	7.4	30
NO_2	27.6	19.9	7.7	26
$N{=}CH_2$	31.3	24.7(±2)[c]	6.6(±2)	30
NO	54.1[e]	37.6	16.5	5[e]

[a]Based upon *C*H chemical shift in 1,3,5-tri-*tert*-butylbenzene 119.4 ppm (24).
[b]Based upon *C*H chemical shift in benzene 128.5 ppm (24) and compilation (20).
[c]Assumed on basis of N=CHPh.
[d]B.G. Gowenlock and A.S.F. Boyd. Unpublished observations.
[e]This work.



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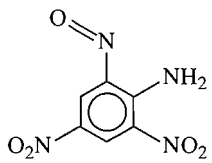

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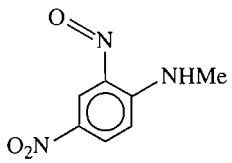

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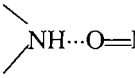
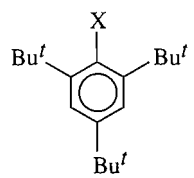
equilibrium position *anti* to the NHMe substituent. Comparison of **5** with **7** suggests that the absence of NO_2 *ortho* to the NHMe removes the steric constraints and allows the NO to rotate freely at room temperature. It should be noted that comparison with *o*-substituted benzaldehyde establishes that this effect on the ^{13}C nmr spectra is absent for the isoelectronic CHO group. A referee has suggested that hydrogen bond formation may take place between the NH and NO groups in compounds **5**, **6**, and **7** assisted by the "acidifying" of the NH by the presence of the nitro group at C5. Such a contribution would, however, orientate the NO group away from C6 and towards C2 because of the



NH···O=N- structural unit. We therefore prefer the explanation of a steric constraint that operates effectively for 5 but is absent for 6 and 7. It is necessary to have further study of related compounds to confirm our preference.

We now turn to the two examples where the bulky *tert*-butyl substituents are placed in both the 2 and 6 positions. The effect on the C-1 chemical shift is considerable and there is no difference between the C-2 and C-6 shifts. As free rotation is ruled out on steric grounds it therefore seems that the orthogonality of the NO group, as proposed originally by Okazaki and Inamoto, is the most probable cause of these effects. To substantiate such considerations it is necessary to compare the substituent chemical shifts for C-X in the molecules **8** and **9** to see whether the variation of X for a wide range of functional groups indicate any



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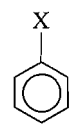

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features of note compared with X-NO. Such considerations were employed by Relles (24) for six different examples of X and in Table 2 we present a considerably expanded series of values.

Inspection of Table 2 shows that the effect on the substituent chemical shifts for X-NO is much greater (16.5 ppm) than for 17 other functional groups (average value 7.2 ppm). The isoelectronic groups CHO and $N{=}CH_2$ together with NNPh are different from NO in that the substituent chemical shift effect is much lower (9.4–6.6 ppm). The effect of 2,4,6-trisubstitution by the *tert*-butyl groups is expected to cause a pronounced twisting of many functional groups out of coplanarity with the ring (Br and CN are obvious exceptions). It should be noted that the inability of TBNB to self-dimerise is due to steric considerations. Cross dimerisation with other C-nitroso compounds has been established (4, 31) and therefore the electronic rearrangements necessary (12, 32) for formation of the $-N_2O_2-$ functions are unaffected by the presumed orthogonality of the NO group in TBNB. This may therefore imply that the unusual effect on the C-1 substituent chemical shift in TBNB arises from the changing interaction of the lone pair of electrons, located primarily on the N atoms, with the π-electrons of the ring.

We note therefore that ^{13}C nmr spectroscopy has revealed three features of unique interest for nitrosobenzene and derivatives thereof, namely, the *syn* effect of in-plane NO, and the orthogonal effect due to steric hindrance, in addition to the dominating effect of the π-electron-attracting NO over other π-electron-attracting groups in the *para* position (5). So far as the last of these effects is concerned, neither CNDO/2 nor STO-3G calculations have been successful in accounting for the difference between the NO group and all other functional groups (33). Theoretical studies for the *syn* effect are limited to the approximate magnetic anisotropy calculations for the nitroso group (1).

There is an STO-3G study of the conformation and charge distributions of a large number of monosubstituted benzenes (34) that is relevant to our study of the orthogonal NO group in TBNB. Hehre, Radom, and Pople point out that whereas the substituent withdraws π-electrons from the ring in planar nitrosobenzene there is π-charge donation from the nitrogen lone pair in the orthogonal form, and the charge alternation is reversed. The authors suggest that this may have interesting consequences in the properties of those nitrosobenzenes constrained to be orthogonal and note the absence of this effect in the orthogonal form of nitrobenzene. In addition to these theoretical calculations Batich and Donald (35) have demonstrated an unusual affect on the N(1*s*) peak in the XPS spectrum of TBNB and, in attempting to correlate this with the orthogonality of the NO group, have shown by CNDO/2 calculations that the charge on the N approximately doubles on going from an in-plane to an orthogonal conformation, while the charge on the O remains the same. These electronic effects may be mirrored by the distinctive difference for NO in the substituent chemical shifts summarised in Table 2.

It is also of interest to note that the orthogonal orientation of the NO group in TBNB implies that in the, yet to be synthesised, analogous molecule 1,3-di-nitroso-2,4,6-tri-*tert*-butylbenzene, atropisomeric forms will exist. These will be (*a*) the two nitroso groups having their O atoms on the same side of the ring and (*b*) the two nitroso groups having their O atoms above and below the plane of the ring.

In principle it would be appropriate to study the ^{13}C nmr spectra of the series of 2,4,6-trialkylnitrosobenzene monomers (alkyl = Me, Et, iPr, *t*Bu) to obtain information on the increasing steric constraints on the NO group. The triisopropylnitrosobenzene has yet to be synthesised and consequently we decided to limit our study to the series of 2,6-dialkylnitrosobenzenes. The first three members of the series form crystalline *trans* dimers and in solution at room temperature there is only a small amount of dissociation to the monomer for the 2,6-dimethyl compound. Heating the sample produces more monomer but decomposition reactions predominate for the ethyl (19) and isopropyl compounds. Consequently it is not possible to achieve the above objective. The ^{13}C nmr spectral data of the dimers are shown in Table 3. These are closely similar to the values predicted from substituent chemical shifts (14, 20).

In conclusion, it may be noted that the dimeric nitroso group does not possess a lone pair of electrons and that, as a consequence of the increase in both the CNO angle and the NO bond length as compared with the monomer, the distance between the O atom and the C-2 atom in the benzene ring will be slightly increased. These considerations encouraged us to study the CPMAS ^{13}C nmr spectrum of solid dimeric 4-bromonitrosobenzene in order to observe whether the splitting of the C-2 and C-6 chemical shifts, characteristic of the *syn* effect in monomeric nitrosobenzenes, would occur. As was to be expected, the compound displayed only four chemical shifts: 140.0 (C-1), 125.1 (C-2), 127.7 (C-3), and 126.4 (C-4) ppm. It is known that in the solid state the benzene rings are tilted only slightly from coplanarity with the $C_2N_2O_2$ central unit (36) and we therefore conclude that the *syn* effect is not a property of the dimeric nitroso functional group. Our studies point therefore to the importance of the nitrogen lone pair in producing the characteristic structural properties of the NO group. More advanced molecular orbital calculations than STO-3G would appear to be necessary to resolve this problem. The experimental techniques of ^{1}H and ^{13}C nmr spectroscopy produce complementary evidence for the *syn* and orthogonal effects of sterically constrained NO groups.

TABLE 3. ^{13}C Chemical shifts for dimeric 2,6-dialkylnitrosobenzenes in $CDCl_3$ solution at 19°C (values in ppm relative to Me_4Si)

Alkyl	C-1	C-2,6	C-3,5	C-4
Me	141.4	132.7	128.9	130.3
Et	140.6	138.3	126.9	130.6
iPr	139.3	143.2	124.6	130.8

Acknowledgements

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1. R. Okazaki and N. Inamoto. J. Chem. Soc. B, 1583 (1970).
2. R.J. Sundberg. Tetrahedron, **23**, 1583 (1967).
3. L.R.C. Barclay, P.G. Khazanie, K.A.H. Adams, and E. Reid. Can. J. Chem. **55**, 3273 (1977).
4. L.R.C. Barclay, D.L. Carson, J.A. Gray, M. Grossman, P.G. Khazanie, J.R. Milton, and C.E. Scott. Can. J. Chem. **56**, 2665 (1978).
5. B.M. Al-Tahou and B.G. Gowenlock. Recl. Trav. Chim.Pays-Bas, **105**, 353 (1986).
6. L. Lunazzi, D. Macciantelli, and G. Placucci. Tetrahedron Lett. **21**, 975, (1980).
7. Y.K. Grishin, N.M. Seryeyev, O.A. Subbotin, and Y.A. Ustynyuk. Mol. Phys. **25**, 297 (1973).
8. V.V. Negrebetskii, A.U. Bokanov, and B.I. Stepanov. Zh. Strukt. Khim. **22**, 88 (1981).
9. M. Cameron, B.G. Gowenlock, and G. Vasapollo. Chem. Soc. Rev. **19**, 355 (1990).
10. M. Cameron, B.G. Gowenlock, R.V. Parish, and G. Vasapollo. J. Organomet. Chem. In press.
11. G.H. Penner and R.E. Wasylishen. Can. J. Chem. **67**, 525 (1989).
12. B.G. Gowenlock and W. Lüttke. Q. Rev. (London), **12**, 321 (1958).
13. R.H. Cox and M. Hamada. Org. Magn. Reson. **12**, 322 (1979).
14. K.G. Orrell, V. Sik, and D. Stephenson. Magn. Reson. Chem. **25**, 1007 (1987).

15. E. Bamberger. Ber. Dtsch. Chem. Ges. **28**, 249 (1895).
16. A. Rising. Ber. Dtsch. Chem. Ges. **35**, 3036 (1902).
17. R. Okazaki, T. Hosagai, E. Iwadare, M. Hashimoto, and N. Inamoto. Bull. Chem. Soc. Jpn. **42**, 3611 (1969).
18. K. Hirota and H.A. Itano. J. Biol. Chem. **253**, 3477 (1978).
19. S.J. Wratten, H. Fujiwara, and R.T. Solsten. J. Agric. Food Chem. **35**, 484 (1987).
20. D.F. Ewing. Org. Magn. Reson. **12**, 499 (1979).
21. J. Kavalek, V. Machacek, V. Sterba, and A. Lycka. Collect. Czech. Chem. Commun. **53**, 1033 (1988).
22. V. Machacek, M.M.M. Hassanien, V. Sterba, and A. Lycka. J. Chem. Soc. Perkin Trans. 2, 867 (1987).
23. V. Machacek, C. Sterba, I. Kolb, and A. Lycka. Collect. Czech. Commun. **53**, 1044 (1988).
24. H.M. Relles. J. Magn. Reson. **39**, 481 (1980).
25. H. Lumbroso, J. Cure, R. Okazaki, A. Ishii, and N. Inamoto. Z. Naturforsch. **40A**, 1157 (1985).
26. J. Koudelka, D. Saman, and O. Exner. Collect. Czech. Chem. Commun. **50**, 208 (1985).
27. E.T.K. Haupt and D. Leibfritz. Spectrochim. Acta A, **45**, 119 (1989).
28. K.S. Dhami and J.B. Stothers. Can. J. Chem. **44**, 2855 (1966).
29. L.R.C. Barclay, J.M. Dust, S. Brownstein, and E.J. Gabe. Org. Magn. Reson. **17**, 175 (1981).
30. G.A. Harff, A. Sinnema, and B.M. Wepster. Recl. Trav. Chim. Pays-Bas, **98**, 71 (1979).
31. K.G. Orrell, D. Stephenson, and J.H. Verlaque. J. Chem. Soc. Perkin Trans. 2, 1297 (1990).
32. T. Minato, S. Yamabe, and H. Oda. Can. J. Chem. **60**, 2740 (1982).
33. G. Butt, R.D. Topsom, B.G. Gowenlock, and J.A. Hunter. Theochem, **164**, 399 (1988).
34. W.J. Hehre, L. Radom, and J.A. Pople. J. Am. Chem. Soc. **94**, 1496 (1972).
35. C.D. Batich and D.S. Donald. J. Am. Chem. Soc. **106**, 2758 (1984).
36. C. Darwin and D.C. Hodgkin. Nature, **166**, 827 (1950).